Unconventional Pairing in Doped Band Insulators on a Honeycomb Lattice : the Role of the Disconnected Fermi Surface and a Possible Application to Superconducting β-MNCl (M=Hf,Zr)

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Abstract. We investigate the possibility of realizing unconventional superconductivity in doped band insulators on the square lattice and the honeycomb lattice, where the latter is found to be a good candidate due to the disconnectivity of the Fermi surface. We propose applying the theory to the superconductivity in doped layered nitride β-MNCl (M =Hf, Zr). Finally, we compare two groups of superconductors with disconnected Fermi surface, β-MNCl and the iron pnictides, which have high T_c despite some faults against superconductivity are present.

keywords: β-MNCl, superconductivity, band insulator, Fermi surface, spin fluctuations, pnictides

1. Introduction

Layered nitride β-MNCl[1] (M =Hf, Zr) doped with carriers is one of the most interesting group of superconductors. The mother compound β-MNCl is composed of alternate stacking of honeycomb MN bilayer and Cl bilayer.[2] This is a band insulator and becomes a superconductor upon doping electrons by Na or Li intercalation. They exhibit relatively high T_c up to $\sim$ 25K for M =Hf and $\sim$ 15K for M =Zr. The bilayer honeycomb lattice structure consisting of M and N (Fig.1) is considered to be playing the main role in the occurrence of superconductivity, and the two dimensional nature of the superconductivity has been revealed by nuclear magnetic resonance[3] and muon spin relaxation studies.[4, 5] Despite the relatively high T_c, experimental as well as theoretical studies indicate extremely low density of states (DOS) at the Fermi level.[6, 7, 8] In fact, they have the highest T_c among materials with the specific heat γ as small as $\sim$ 1mJ/molK^2. The electron phonon coupling is also estimated to be weak,[6, 8, 9, 10] and the isotope effect is found to be small.[11, 12] In the superconducting state, the

density of states recover rapidly upon increasing the magnetic field,[7] suggesting some kind of anisotropic pairing. As for the doping dependence, the DOS at the Fermi level stays nearly constant, but, for Li_xZrNCl, T_c shows an increase upon lowering the carrier concentration until a sudden disappearance of the T_c and a superconductor-insulator transition is observed.[13] On the other hand, in Li_xHfNCl, T_c stays nearly constant for the whole doping range $x < 0.5$.[14] Furthermore, for Li_xHfNCl, an intercalation of organic molecules tetrahydrofuran (THF) between the layers is found to enhance T_c. [14] While these experiments suggest that some kind of unconventional pairing mechanism may be at work, tunneling spectroscopy experiments on the other hand find an s-wave like, fully open gap.[15] Specific heat measurements also suggest an s-wave like gap, but again the doping dependence of the magnitude of the gap is unusual. In the underdoped regime, the gap is large, while the gap becomes small as the doping level is increased, varying from a "strong coupling" to an "extremely weak coupling" superconductor.[17]

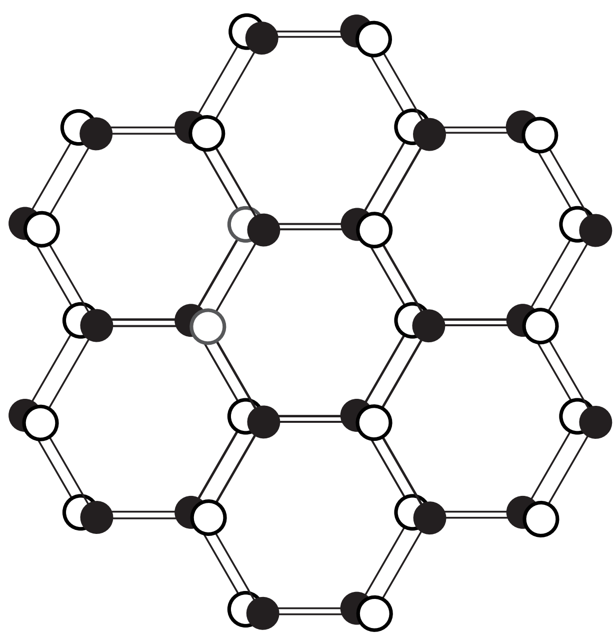


Figure 1. The bilayer honeycomb lattice is shown. The black and white circles represent M(=Hf, Zr) and N, respectively.

In the present study, we first generally study the possibility of unconventional superconductivity by doping band insulators on a square or honeycomb lattice.[16] We find that the honeycomb lattice is a good candidate for realizing such a possibility, where the disconnectivity of the Fermi surface plays a role. Secondly, we consider applying the theory to β-MNCl. The two bands sitting closest to the Fermi level in the first principles band calculation[8] can roughly be reproduced by a *single* honeycomb lattice model, where the above general theory can be applied. Finally, we compare two groups of superconductors with disconnected Fermi surface, β-MNCl and the iron pnictides, which have high T_c despite some faults against superconductivity are present.

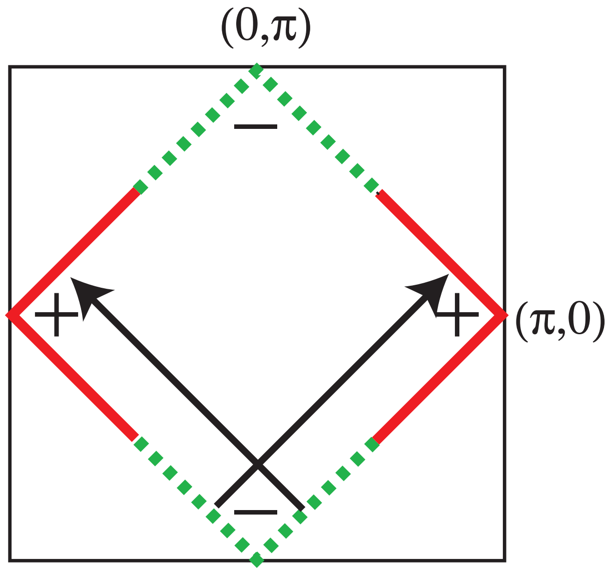


Figure 2. An explanation of the d-wave superconductivity due to spin fluctuations on the square lattice. The arrow represents the wave vector $\boldsymbol{Q}$ at which the spin fluctuations develop. The solid (dashed) lines are the portions of the Fermi surface where the gap has a positive (negative) sign.

2. Square lattice

Hubbard Model is a model that considers the on-site repulsive interaction U on a tight binding model. Let us start with the Hubbard model on a square lattice, where we consider only the nearest neighbor t as the hopping integral. When the band filling n (=number of electrons/number of sites) is near half-filling ($n \sim 1$), strong antiferromagnetic spin fluctuations arise, and the possibility of d-wave superconductivity mediated by these spin fluctuations has been discussed for the past several decades. The d-wave superconductivity can be understood as follows. Generally, superconductivity occurs due to pair scattering mediated by the pairing interaction $V(\boldsymbol{q})$. The gap equation can be written as

$$\Delta(\boldsymbol{k}) = -\sum_{\boldsymbol{k}'} \frac{\tanh[E(\boldsymbol{k}')/k_B T]}{2E(\boldsymbol{k}')} V(\boldsymbol{k}' - \boldsymbol{k}) \Delta(\boldsymbol{k}'), \tag{1}$$

where Δ is the gap, E is the quasiparticle dispersion, and T is the temperature. When the spin singlet pairing interaction is mediated by spin fluctuations, $V(\boldsymbol{k})$ is positive and takes large values at large $\boldsymbol{Q}$, where the spin fluctuation develops. So in the case of the square lattice, where the spin fluctuations develop near $\boldsymbol{Q} = (\pi, \pi)$, we have to change the sign of the gap between the wavevectors $\sim (\pi, 0)$ and $\sim (0, \pi)$ in order to have a finite Δ as a solution for the gap equation, which results in a d-wave gap as shown in Fig.2. By applying fluctuation exchange (FLEX) approximation to this system, which is a kind of self-consistent perturbation theory that collects random phase approximation type diagrams, we can obtain the Green's function and the spin

susceptibility.[18] These can be plugged into the Eliashberg equation, whose solution gives a d-wave superconductivity with a T_c of the order of $0.01t$, where t is the nearest neighbor hopping integral (if $t \sim 1$eV, T_c is of the order of 100K).

Now, the square lattice (with only the nearest neighbor hopping) is a bipartite lattice which can be separated into A and B sublattices. Let us see what happens to the superconductivity if we introduce a level offset Δ between A and B lattices. The introduction of Δ opens up a gap at the center of the band, so this amounts to investigating the possibility of unconventional superconductivity by doping carriers in band insulators (Fig.3(a)). As shown in Fig.4, we find that the introduction of Δ rapidly suppresses superconductivity. Thus, in the case of the square lattice, chances for realizing unconventional superconductivity in the above sense are small.

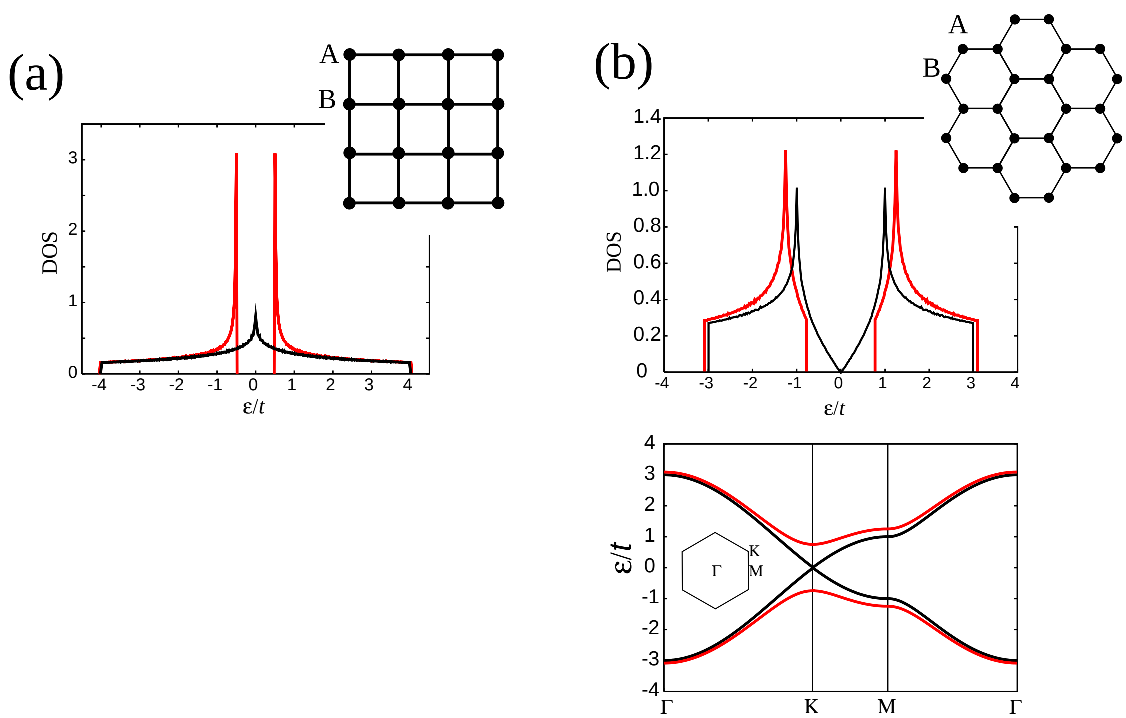


Figure 3. (a) The density of states for the square lattice with $\Delta = 0$ (black) and $\Delta = t$ (red).(b) The density of states (upper) and the band dispersion (lower) for the honeycomb lattice with $\Delta = 0$ (black) and $\Delta = 1.5t$. The hexagonal Brillouin zone of the honeycomb lattice is shown in the inset of the lower panel.

3. Honeycomb lattice

Now, let us compare the above result for the square lattice with those for another two dimensional bipartite lattice, namely, the honeycomb lattice. The honeycomb lattice is a system with two sites in a unit cell, in which the two bands make point contact at K and K' points of the Brillouin zone, resulting in a zero gap density of states (Fig.3(b)). We show in Fig.5(a) the maximum value of the spin susceptibility as a

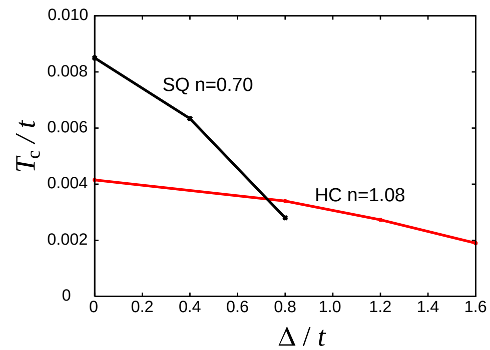


Figure 4. T_c as functions of the level offset Δ obtained by FLEX+Eliashberg equation for the square lattice with $U = 6t$, $n = 0.7$ (black) or for the honeycomb lattice with $U = 6t$ and $n = 1.08$ (red).

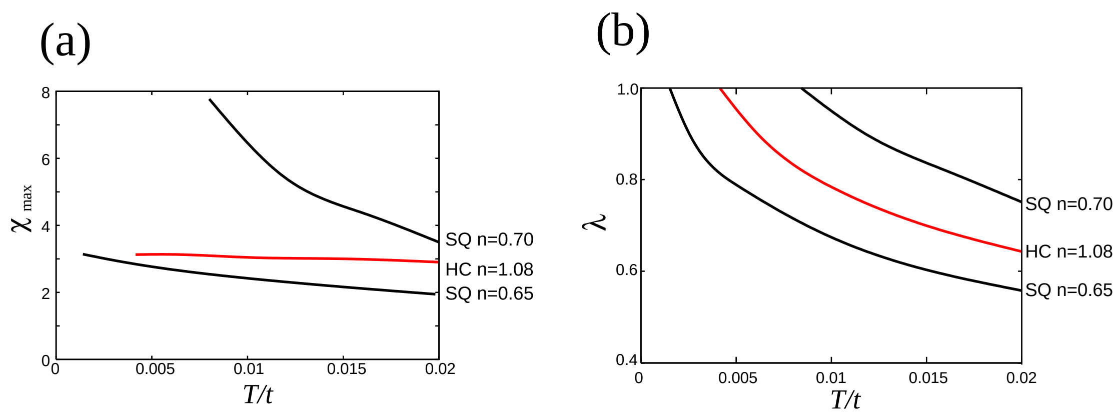


Figure 5. (a) The maximum value of the spin susceptibility as functions of temperature obtained by FLEX for the square lattice with $n = 0.7$ or $n = 0.65$ and for the honeycomb lattice for $n = 1.08$. $U = 6t$ in all cases. HC and SQ stand for the honeycomb and the square lattices, respectively. (b) The eigenvalue of the linearized Eliashberg equation with the same parameter values as in (a). The temperature at which $\lambda = 1$ is the T_c.

function of temperature for the band filling of $n = 1.08$, which corresponds to a small amount of electron doping. Surprisingly, we find that the spin susceptibility is nearly independent of T, which is in sharp contrast with the case of the square lattice. For example, for the square lattice with $n = 0.7$, which is already substantially away from half-filling, we still have a strong enhancement of the spin susceptibility upon lowering the temperature. With further hole doping to $n = 0.65$, the spin susceptibility is suppressed, but even in that case, there is a moderate increase of the spin susceptibility upon lowering the temperature. In Fig.5(b), we show the eigenvalue λ of the linearized Eliashberg equation as functions of temperature. T_c is the temperature where λ reaches unity. The density of states at E_F is nearly the same for the square lattice with $n = 0.65$ and the honeycomb lattice with $n = 1.08$, and also the spin susceptibility has similar

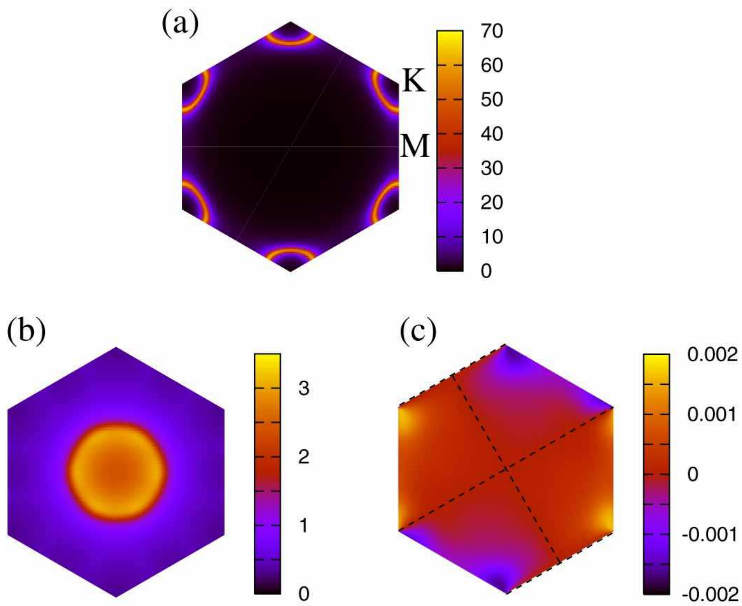


Figure 6. The contour plots of the FLEX result at the lowest Matsubara frequency for the honeycomb lattice in the hexagonal Brillouin zone with $U = 6t$, $n = 1.08$, and $T = 0.01t$ (a) The Green's function of the upper band squared, (b) the spin susceptibility, (c) the superconducting gap function.

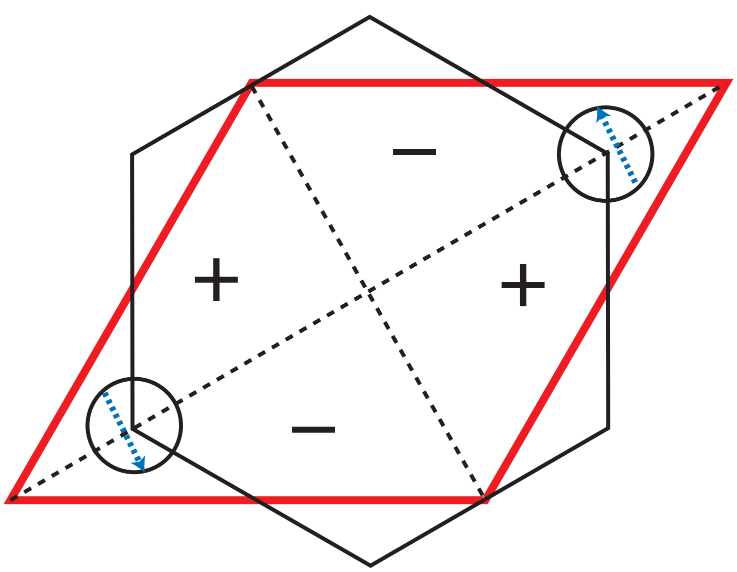


Figure 7. The Fermi surface (the two circles) and the sign of the gap function are schematically shown in the extended zone scheme. The dashed arrows represent the wave vectors at which the spin fluctuations develop.

values at low temperature, but still, the honeycomb lattice has larger λ and higher T_c. Thus, the Hubbard model on the honeycomb lattice has relatively high T_c despite the low density of states and the weak and temperature independent spin fluctuations.

Fig.6 shows the contour plot of the Green's function squared, whose ridge

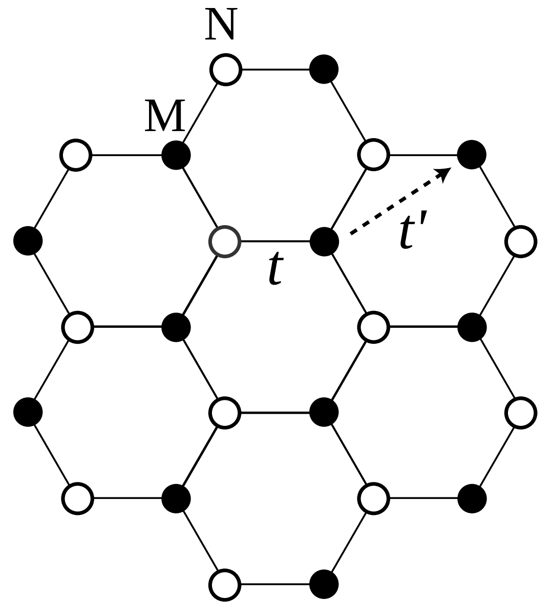
corresponds to the Fermi surface. We see here two disconnected pieces of the Fermi surface. The spin susceptibility is maximized at wave vectors that bridge the opposite sides of each pieces of the Fermi surface. As can be seen more clearly in Fig.7, the gap has a d-wave form, where the gap changes sign across the wave vector at which the spin susceptibility is maximized. Here, note that one of the nodes of the gap do not intersect the Fermi surface because of its disconnectivity, which may be one reason why superconductivity is favored despite the low density of states and the weak spin fluctuations. By symmetry, there are two degenerate d-wave gaps (say, d_{xy} and $d_{x^2-y^2}$, or any two linearly independent combinations), and the most probable form of the gap below T_c is the form $d + id$, where the two d-wave gaps mix with a phase shift of $\pi/2$. Since the two d-wave gaps have nodal lines at different positions, this kind of mixture leads to a gap that has a finite absolute value on the entire Fermi surface. An important point is that if such a state is realized, the time reversal symmetry should be broken.

Now we introduce the level offset between A and B sites as we did for the square lattice. In this case also, a band gap opens in the center (Fig.3(b)), so we once again investigate the possibility of superconductivity by doping band insulators. In this case, we find that superconductivity is relatively robust against the introduction of Δ. This may be because the density of states is already low in the original honeycomb lattice, so that the introduction of Δ does not affect superconductivity so much.

4. Application to β-MNCl

We now consider applying the above theory to β-MNCl. Although β-MNCl has a bilayer honeycomb lattice structure, we find that the two bands closest to E_F obtained in the first principles calculation [8, 10, 19, 20] can roughly be reproduced by a *single* layer honeycomb lattice model consisting of alternating "M" and "N" orbitals with a level offset as shown in Fig.8. Here we take $t = 1.2$eV, $\Delta/t = 2.7$, and $t'/t = 0.35$. If we consider on-site repulsive interaction $U = 6t$ on both M and N orbitals,[21] the model is similar to the one studied in section 2, except that distant hopping integrals t' have to be considered so as to reproduce the first principles band structure. Consequently, within the FLEX+Eliashberg equation approach, we obtain relatively high T_c of around 30K as shown in Fig.9.

Now we compare the present scenario with the experiments for β-MNCl. As mentioned in the Introduction, relatively high T_c is obtained despite the extremely low density of states and the weak electron phonon coupling,[6, 7, 9, 8, 10] which can be explained within the present theory. The isotope effect is small,[11, 12] which again seems consistent since the the present pairing mechanism is purely electronic. The cointercalation of THF molecules enhances T_c,[14] and this also seems to be understandable within this kind of spin fluctuation mediated pairing, where the quasi two dimensionality is favored as discussed generally in refs.[22, 23]. As for the pairing symmetry, a fully open gap is observed in the experiments,[15] and this is consistent with the present scenario provided that the $d + id$ state is realized. It is hence interesting to



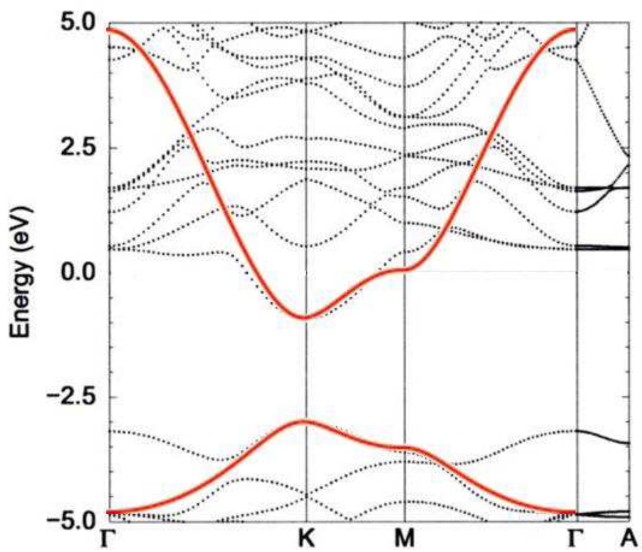


Figure 8. Upper panel: the tightbinding model considered for β-MNCl. Lower panel: the first principles band calculation taken from ref.[8] and the band dispersion of the tightbinding model.

investigate experimentally the possibility of time reversal symmetry breaking in the superconducting state of this material. The rapid recovery of the specific heat by applying the magnetic field,[7] and also the unusual doping dependence of both the T_c and the magnitude of the gap[13, 14, 17] remain as an interesting future problem.

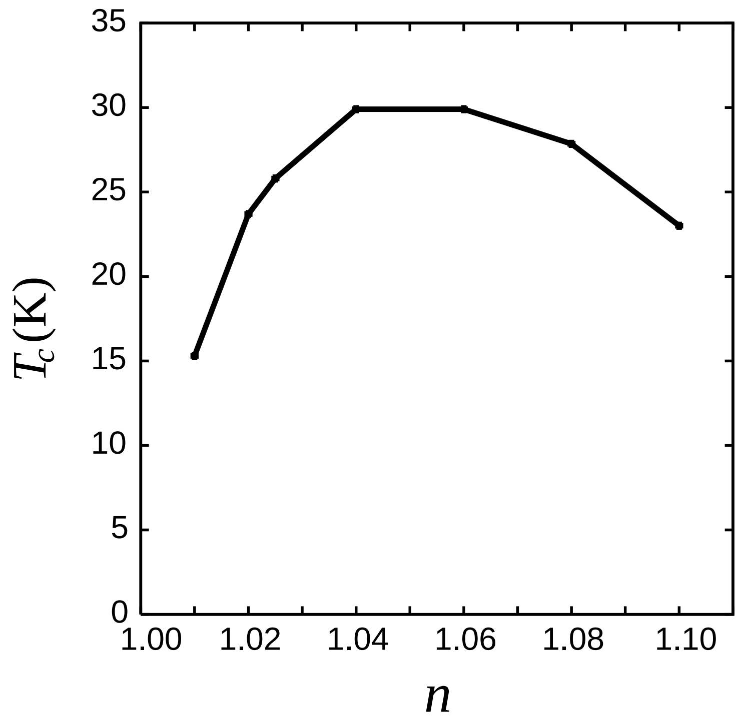


Figure 9. T_c plotted as a function of the band filling for the model shown in Fig.8.

5. Superconductivity in systems with disconnected Fermi surface

Finally, let us go back to the d-wave superconductivity on the square lattice. As mentioned, T_c obtained by FLEX is the order of $0.01t$, where t is the hopping integral. This can correspond to a high T_c in actual materials because t can be of the order of electron volt, but still this is low compared to the original energy scale t. There are several reasons for the "low" T_c, and one of them is that we have to have nodes of the gap *intersecting* the Fermi surface because sign change of the gap is required in the case of spin fluctuation mediated pairing. In this context, we proposed some time ago that if there are disconnected pieces of Fermi surface nested to some extent, we can change the sign of the gap between the disconnected peaces without the nodes intersecting the Fermi surface, and this can result in a high T_c superconductivity.[24] An example of such a Fermi surface is shown in Fig.10. Possibilities of the disconnected Fermi surface playing important role in the occurrence of superconductivity or the determination of the pairing symmetry have been discussed for a cobaltate Na_xCoO_2[25] and an organic superconductor $(TMTSF)_2X$.[26]

Quite recently, superconductivity has been found in iron-based pnictides by Hosono and coworkers.[27] The highest T_c of this series of materials have reached 55K.[28] Band calculations show that there are several disconnected pieces of the Fermi surface in this material,[29] where spin fluctuations can arise due to the nesting between them.[30] According to our Eliashberg theory calculation that takes into account such kind of spin

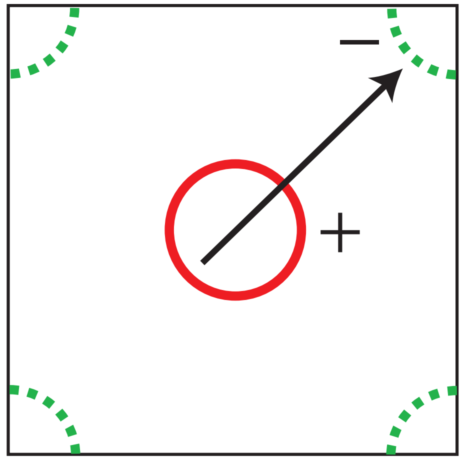


Figure 10. An example of fully open sign reversing gap on a disconnected Fermi surface is shown. The arrow shows the nesting vector at which the spin fluctuations develop.

fluctuations,[31] the gap changes sign across the nesting vector of the Fermi surface, and the magnitude of the gap is especially large on the portion of the Fermi surface where the $d_{x^2-y^2}$ orbital character is strong as shown in Fig.11. The nearest neighbor hopping of this orbital is about 0.15eV, which is quite small, and the experimentally observed maximum $T_c = 55$K corresponds to about $0.04t$ which is higher than that can be reached in the single band square lattice.

So the two groups of materials seem to exhibit high T_c despite some kind of faults against superconductivity are present: for β-MNCl, relatively high T_c is obtained despite the extremely low DOS and the weak spin fluctuations (and electron-phonon coupling), while for the pnictides, high T_c is obtained despite the low energy scale of the main band, and also competing spin and charge fluctuations due to the multiplicity of the orbitals. The disconnectivity of the Fermi surface may be one good reason why these faults are overcome. In the future, there may a possibility that we can get higher T_c by realizing disconnected Fermi surface on more ideal situations.

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References

[1] S. Yamanaka *et al.*, Nature **392**, 580 (1992).
[2] S. Shamoto *et al.*, Physica (Amsterdam) **402C**, 283 (2004).
[3] H. Tou *et al.*, Phys. Rev. B **63**, 020508 (2000).
[4] Y. J. Uemura *et al.*, Physica (Amsterdam) **289-290B**, 389 (2000).
[5] T. Ito *et al.*, Phys. Rev. B **69**, 134522 (2004).
[6] H. Tou *et al.*, Phys. Rev. Lett. **86**, 5775 (2001).

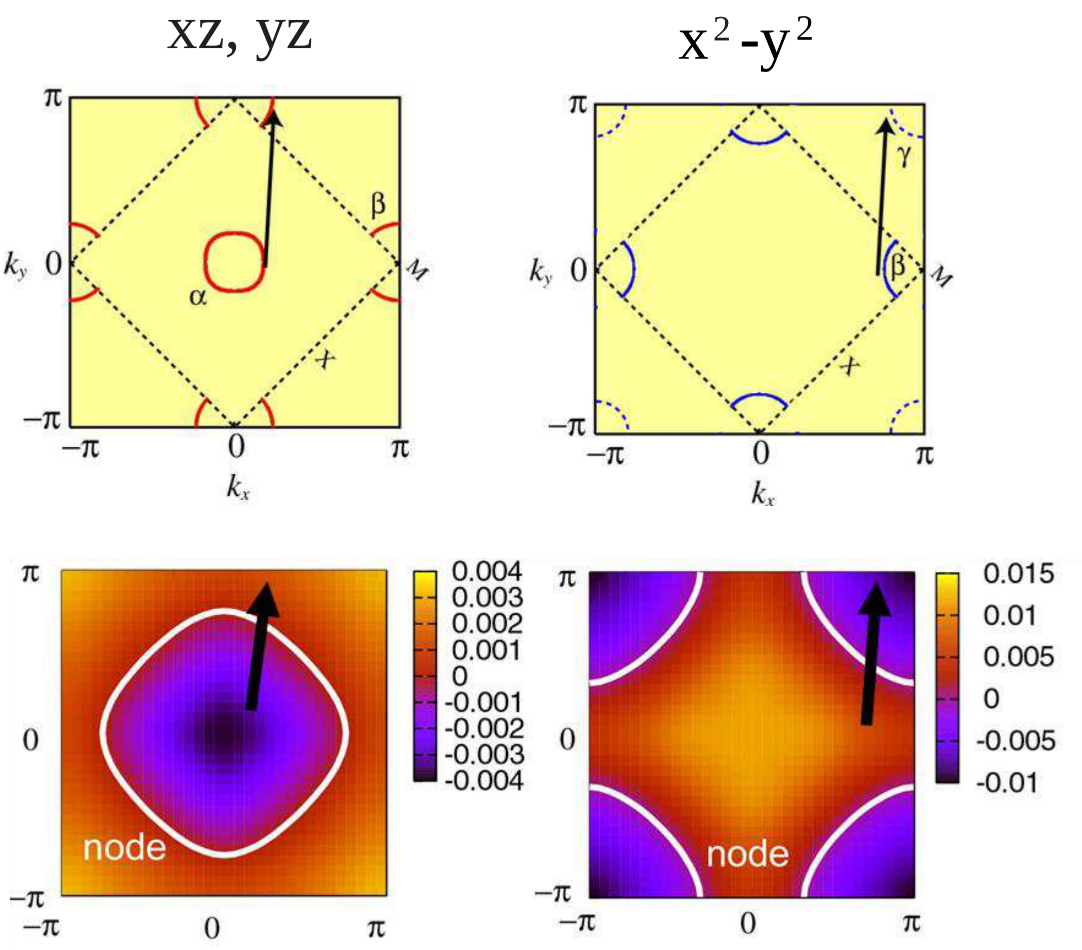

Figure 11. Upper panels : the portions of the Fermi surface of iron pnictides with strong d_{xz}, d_{yz} (left) or $d_{x^2-y^2}$ (right) orbital character. The dashed curve around (π, π) (at the corners of the Brillouin zone) is the portion where a flat portion of the band lies very close to the Fermi level, although it does not actually produce a Fermi surface. The arrows show the nesting vector of the Fermi surface. Lower panels: the gap function for the d_{xz}, d_{yz} (left) or $d_{x^2-y^2}$ (right) orbitals.

[7] Y. Taguchi, M. Hisakabe, and Y. Iwasa, Phys. Rev. Lett. **94**, 217002 (2005).
[8] R. Weht *et al.*, Europhys. Lett. **48**, 320 (1999).
[9] A. Kitora, Y. Taguchi, and Y. Iwasa, J. Phys. Soc. Jpn. **76**, 023706 (2007).
[10] R.Heid and K.P.Bohnen, Phys. Rev. B **72**, 134527 (2005).
[11] H. Tou *et al.*, Phys. Rev. B **67**, 100509 (2003).
[12] Y. Taguchi *et al.*, Phys. Rev. B **76**, 064508 (2007).
[13] Y. Taguchi *et al.*, A. Kitora, and Y. Iwasa, Phys. Rev. Lett. **97** (2006) 107001.
[14] T. Takano, T. Kishiume, Y. Taguchi, and Y. Iwasa, Phys. Rev. Lett. **100**, 247005 (2008).
[15] T. Ekino *et al.*, Physica C **388-389**, 573 (2003); Physica B **328**, 23 (2003).
[16] Theoretically, a possibility of unconventional pairing mediated by charge fluctuations has been proposed in A. Bill *et al.*, Phys. Rev. B **66** 100501(R) (2002).
[17] Y. Kasahara *et al.*, preprint, Proceedings of the LT25 conference.
[18] N.E. Bickers, D.J. Scalapino, and S.R. White, Phys. Rev. Lett. **62**, 961 (1989).

[19] I. Hase and Y. Nishihara, Phys. Rev. B **60**, 1573 (1999).
[20] H. Sugimoto and T. Oguchi, J. Phys. Soc. Jpn. **73**, 2771 (2004).
[21] Generally, the on-site repulsion on the M site and N site can be different, but here we assume them to be equal for simplicity.
[22] R. Arita, K. Kuroki, and H. Aoki, Phys. Rev. B **60**, 14585 (1999).
[23] P. Monthoux and G.G. Lonzarich, Phys. Rev. B **63**, 054529 (2001).
[24] K. Kuroki and R. Arita, Phys. Rev. B **64**, 024501 (2001); K. Kuroki *et al.*, Phys. Rev. B **66**, 184508 (2002).
[25] K. Kuroki *et al.*, Phys. Rev. B **73**, 184503 (2006).
[26] K. Kuroki, R. Arita, and H. Aoki, Phys. Rev. B **63**, 094509 (2001).
[27] Y. Kamihara *et al.*, J. Am. Chem. Soc. **130**, 3296 (2008).
[28] Z.-A. Ren *et al.*, Chin. Phys. Lett. **25**, 2215 (2008).
[29] D.J. Singh and M.-H. Du, Phys. Rev. Lett. **100**, 237003 (2008).
[30] I.I. Mazin *et al.*, Phys. Rev. Lett. **101**, 057003 (2008).
[31] K. Kuroki *et al.*, Phys. Rev. Lett. **101**, 087004 (2008).